Electronic Supplementary Information

Synthesis of $C_{27}H_{27}Na_2O_{16.5}Zn_2$ (**1**)

A mixture of zinc acetylacetonate hydrate (1.0 mmol), NaOH (2.0 mmol) and 5-methylisophthalic acid (1.5 mmol) in 12 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 20 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 180□ for three days under autogenously pressure. After the reaction mixture have slowly cooled down to room temperature, colorless sheet crystals of **1** are filtered off, washed with distilled water, and dried in air. Yield: ~90%. Elemental analysis (%) for $C_{27}H_{27}Na_2O_{16.5}Zn_2$:calcd. C 40.93, H 3.44, Na 5.80, Zn 16.51; found C 40.89, H 3.37, Na 5.72, Zn 16.42. IR (KBr pellet, cm-1): 3414 m, 1622 s, 1568 s, 1426 m, 1360 s, 1245 m, 1140 m, 1116m , 1038m, 803m, 776m, 734m, 607m.

Synthesis of $C_{54}H_{52.5}K_{1.5}O_{32}Zn_5$ (**2**)

A mixture of zinc acetylacetonate hydrate (1.0 mmol), KOH (2.0 mmol) and 5-methylisophthalic acid (1.5 mmol) in 12 mL H_2O are stirred for 10 min at room temperature. The mixture is then transferred into a 20 mL, Teflon-lined stainless-steel vessel. The mixture is heated at 180□ for three days under autogenously pressure. After the reaction mixture has slowly cooled down to room temperature, colorless sheet crystals of **2** are filtered off, washed with distilled water, and dried in air. Yield: ~85%. Elemental analysis (%) for $C_{54}H_{52.5}K_{1.5}O_{32}Zn_5$:calcd. C 40.56, H 3.31, K 3.67, Zn 20.45; found C 40.25, H 3.35, K 3.58, Zn 20.39. IR (KBr pellet, cm-1): 3400 m, 1625 s, 1578 s, 1429 m, 1368 s, 1242 m, 1143 m, 1113m , 1041m, 1007m, 942m, 800m, 776, 725, 607m.

Crystal structure determination and refinement

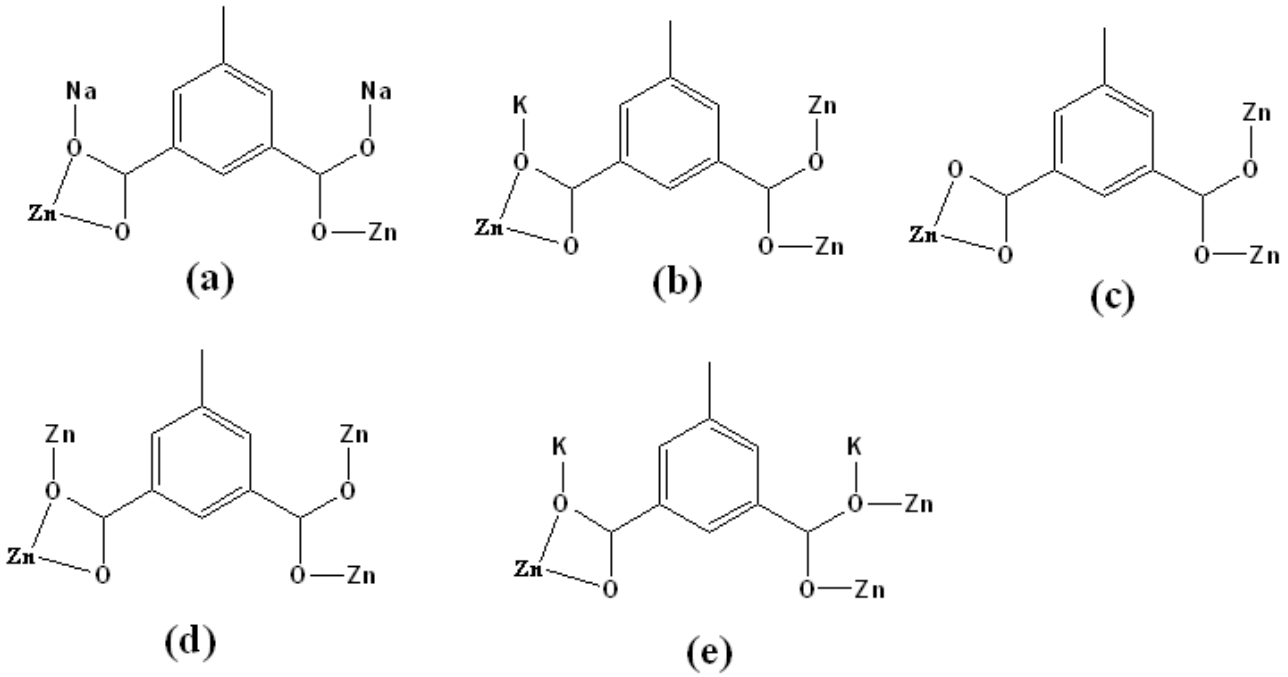
Crystal data of compounds **1** and **2** are collected on a Bruker SMART APEX CCD-based diffractometer ($Mo_{K\alpha}$ radiation,λ=0.71073 Å) at 25℃. The structures are solved by direct method and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. All of the non-hydrogen atoms are refined anisotropically. The organic hydrogen atoms are generated geometrically; the aqua hydrogen atoms are located from difference maps and refined with isotropic temperature factors. It is noticeable that the refinement has been done without the H atoms at O8, O9 and O10/O10' for compound **1**, and the missing H atoms are added in the formula, formula weight etc. For compound **2**, the refinement has been done without the H atoms at O27 and O28, and the missing H atoms are also included in the formula, formula weight etc.

Notice: Typical hydrothermal reactions of inorganic zinc salts (such as zinc acetate, sulfate, chloride and nitrate) in the presence of 5-methylisophthalic acid and NaOH (KOH) only afford to 5-methylisophthalic acid crystalline products or unspecific white precipitates, which may be due to the fast rate of the reaction between Zn(II) ions and mip ligands. When only the zinc salts are substituted with the zinc acetylacetonate hydrate the same reaction produces colorless sheet crystals in very good yields. It shows that the acetylacetonate groups in the reactive system do play a key role in directing synthesis of the MOFs.

Tabl. S1 A summary of the crystallographic data for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{27}H_{27}Na_2O_{16.5}Zn_2$	$C_{54}H_{52.5}K_{1.5}O_{32}Zn_5$
Formula weight	792.21	1598.96
Temperature/ K	298(2)	298(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	$Pna2_1$
a / Å	7.1319(14)	14.1795(3)
b / Å	24.327(5)	23.7646(5)
c / Å	18.849(4)	18.7113(5)
α / deg	90	90
β /deg	90	90
γ / deg	90	90
Volume/ $Å^3$	3270.3(11)	6305.1(3)
Z	4	4
ρ_{cal} /g·cm^{-3}	1.609	1.684
μ /mm^{-1}	1.568	2.066
F (000)	1612	3244
Crystal size/ mm	0.09×0.08×0.06	0.11×0.09×0.08
Limiting indices	-8<=h<=8, -18<=k<=28, -22<=l<=22	-16<=h<=16, -27<=k<=28, -22<=l<=21
Reflections collected	14924	41659
Independent refl.	2942 [*R* (int) = 0.0737]	10761 [*R* (int) = 0.0663]
GOF	1.047	1.038
Final *R* indices	*R*1 = 0.0651	*R*1 = 0.0557
[*I*>2σ(*I*)]	*wR*2 = 0.1675	*wR*2 = 0.1485
R indices	*R*1 = 0.1030	*R*1 = 0.0811
All data	*wR*2 = 0.1974	*wR*2 = 0.1674

Chart S1 Diverse coordination modes of mip (mip=5-methylisophthalate dianion).



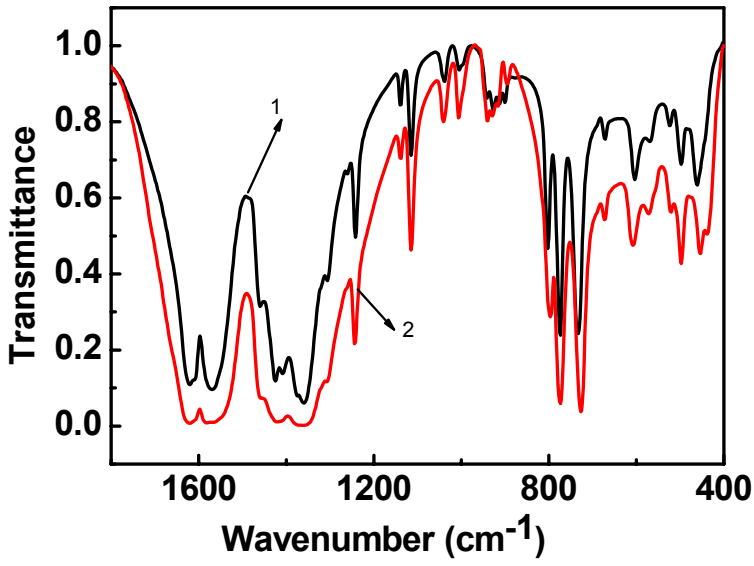


Fig. S1 The FT-IR spectra for **1** and **2**

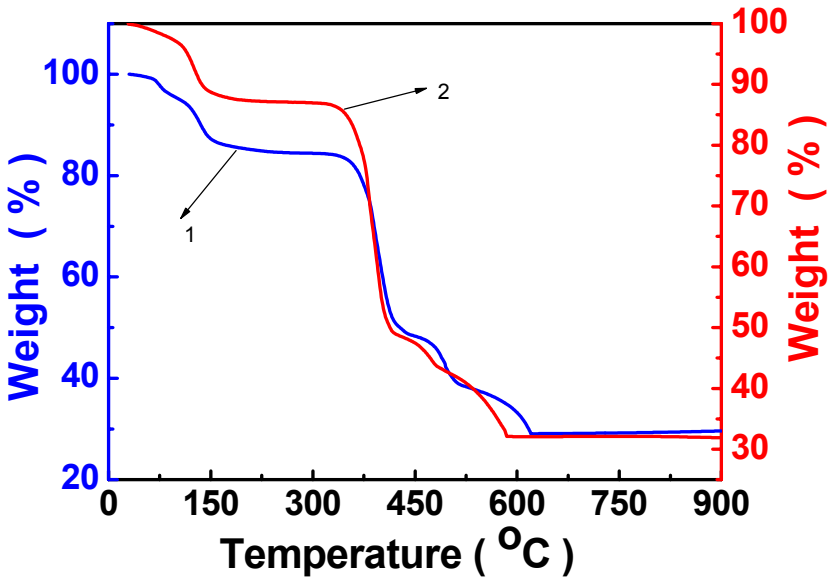


Fig. S2 TG curves for **1** and **2**

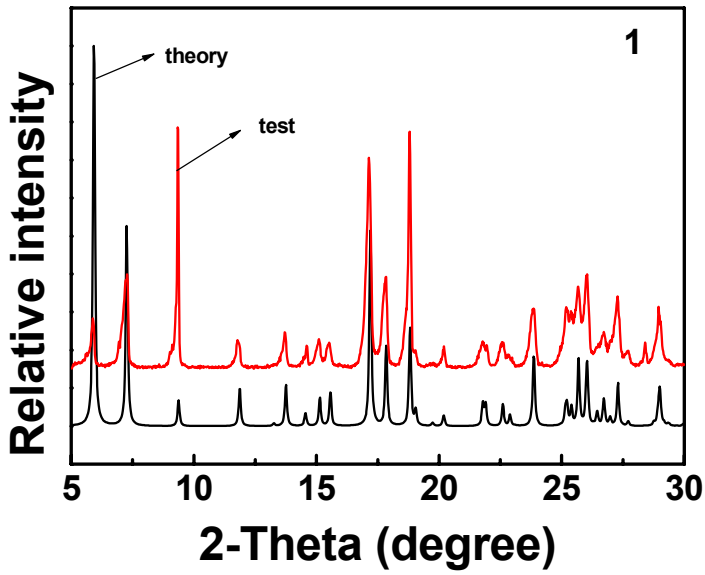


Fig. S3 XRPD patterns of the simulated and as-synthesized compound **1**

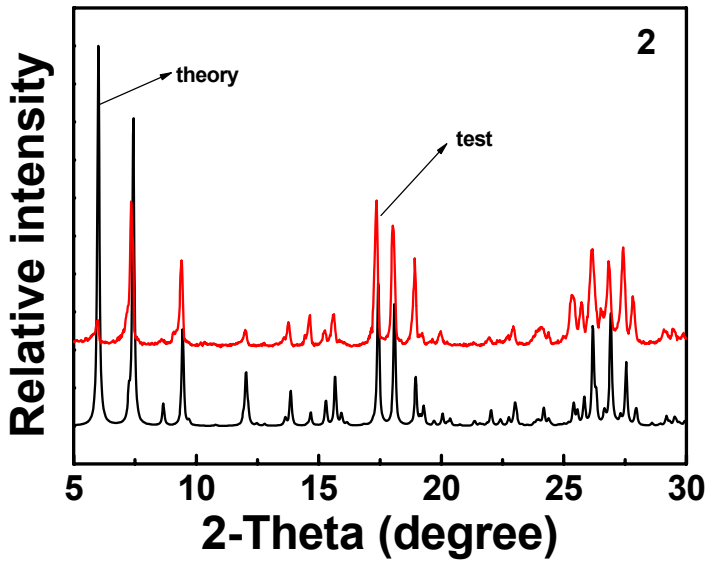


Fig. S4 XRPD patterns of the simulated and as-synthesized compound **2**

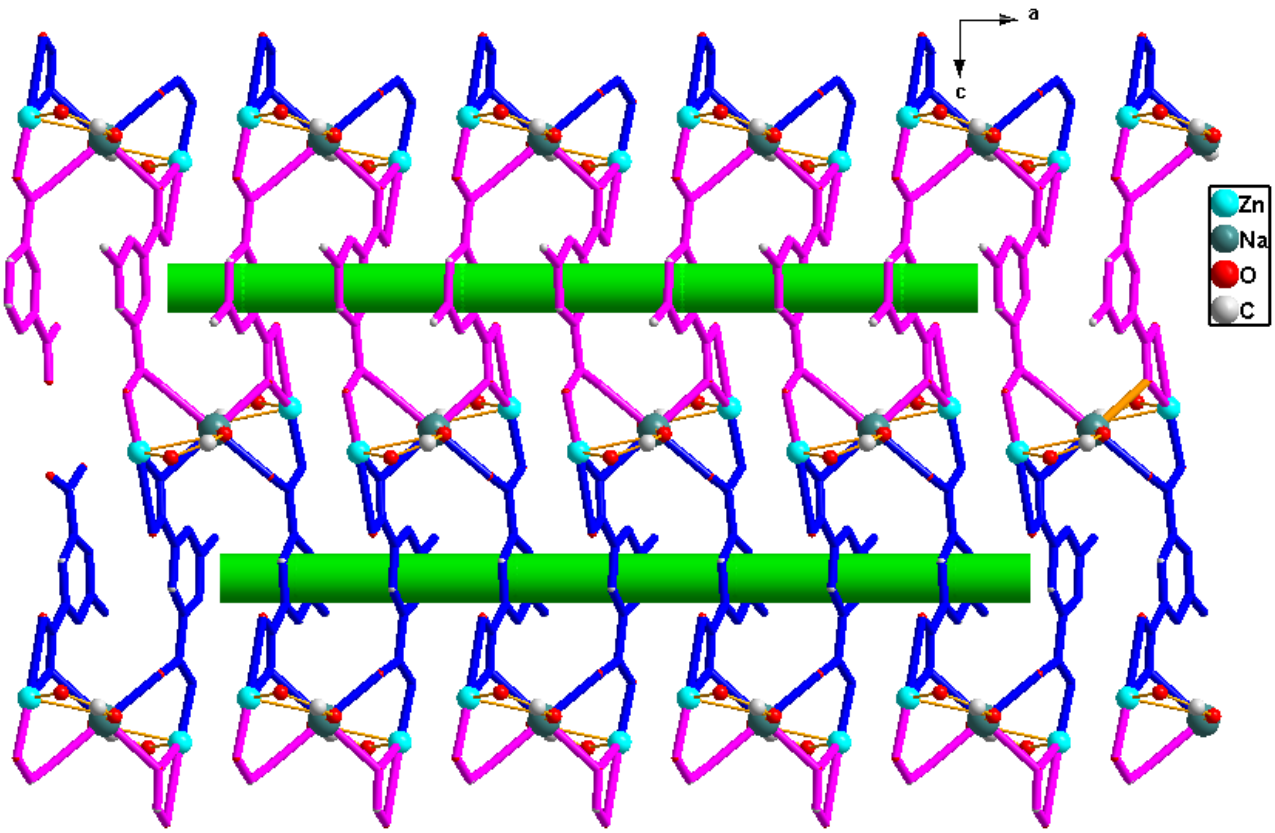


Fig. S5 1D left-and right-handed helical chains constructed from pairs of the adjacent $Zn_2Na(COO)_6$ SUBs and eight mip ligands for **1**

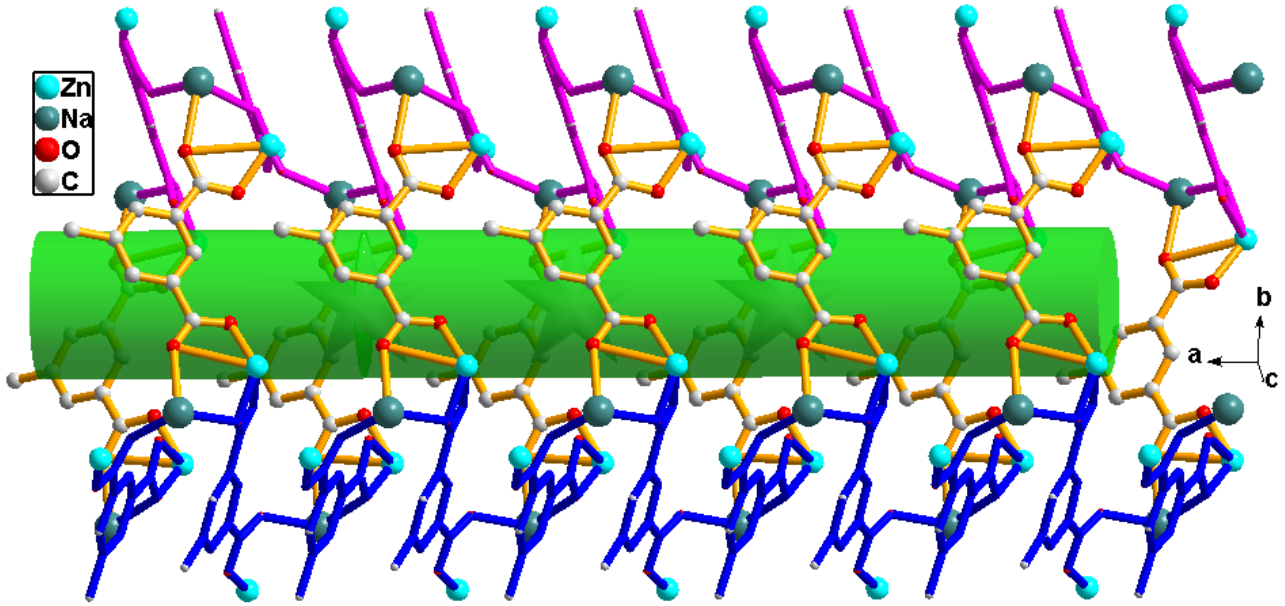


Fig. S6 1D nanotubular helical channels with the hydrophilic character for **1**

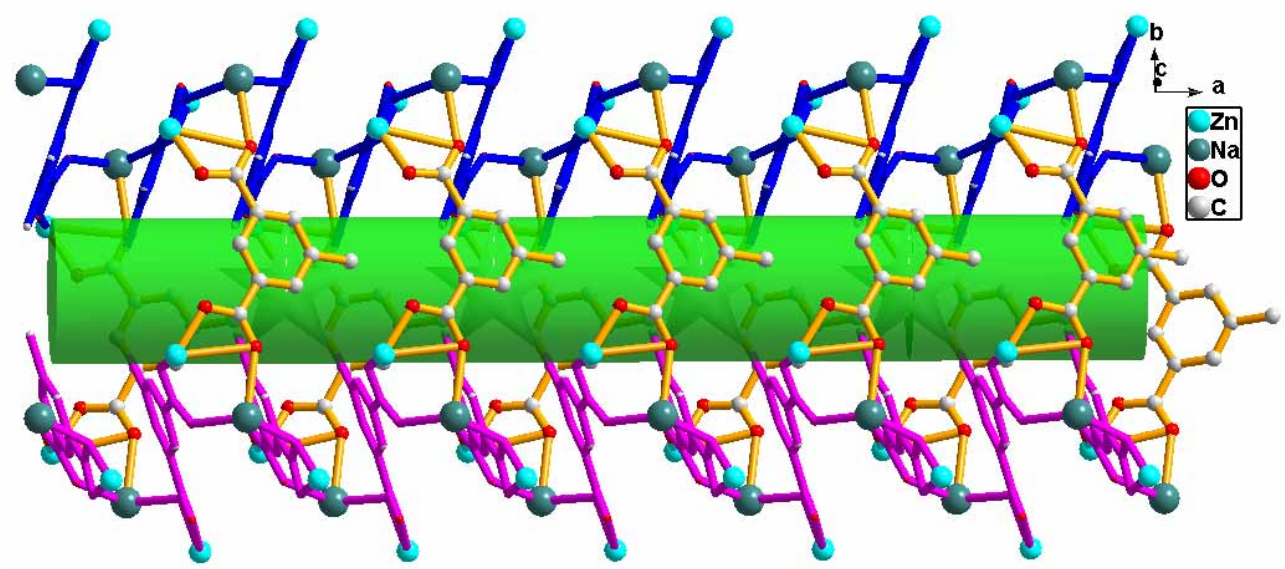


Fig. S7 1D nanotubular helical channels with the hydrophobic character for **1**

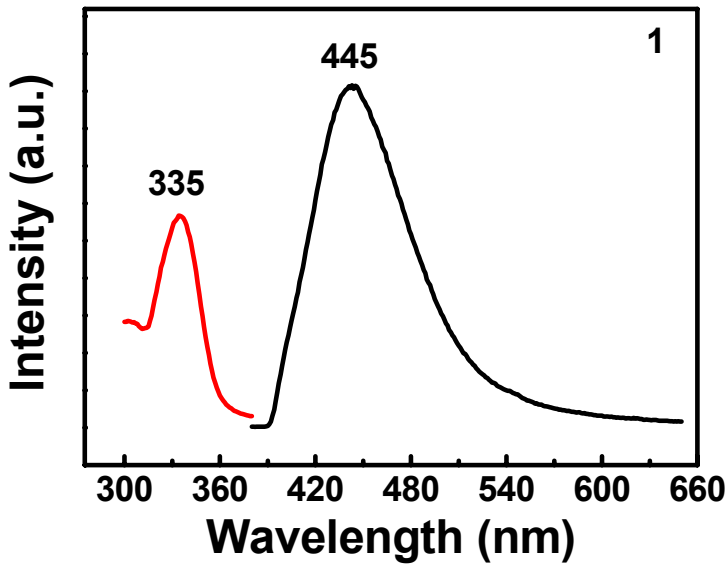


Fig. S8 Excitation (left) and emission (right) spectra of **1**

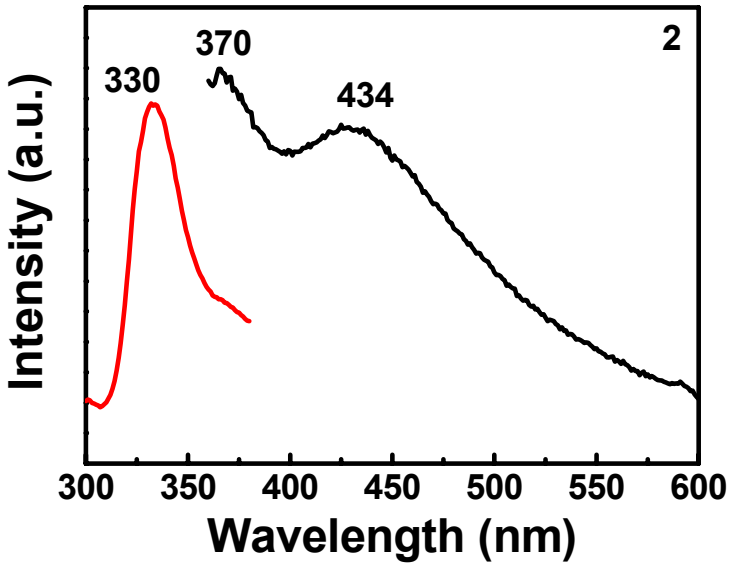


Fig. S9 Excitation (left) and emission (right) spectra of **2**

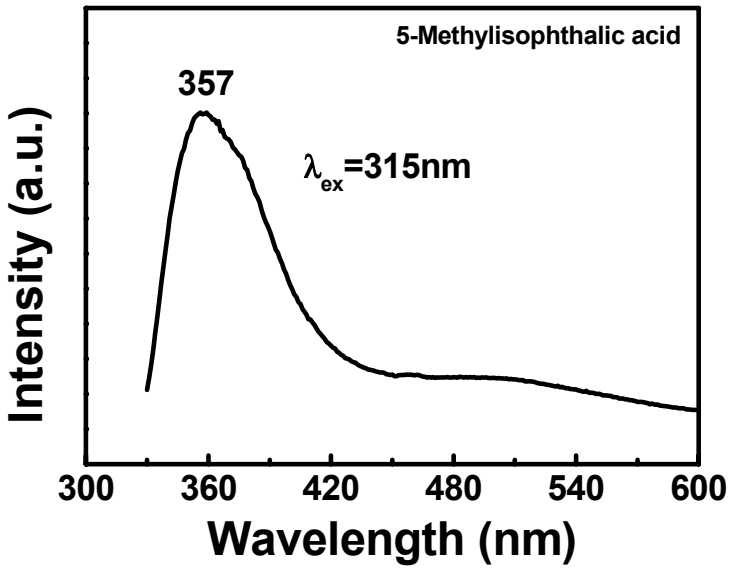


Fig. S10 Emission spectra of 5-Methylisophthalic acid excited at 315 nm